

PATENT ABSTRACTS OF JAPAN

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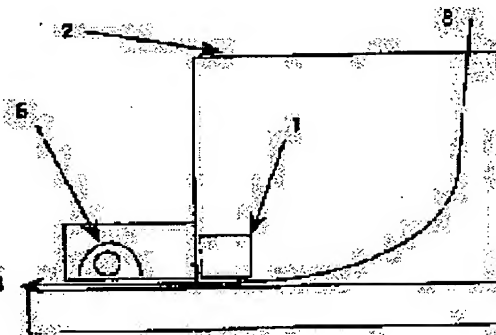
(72)Inventor : NOGUCHI HIROMICHI

(54) INK JET PRINTING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an ink jet printing method by which it is possible to increase the adhesion of ink to a material to be printed after curing and print an image with high transparency when the material to be printed is light-transmissible and print an image with high gloss and chroma when the material is light-reflective.

SOLUTION: Ink jet printing is performed on a material to be printed 3 using ink containing at least, pigment, a water-soluble ultraviolet polymerizable substance and a water-soluble photopolymerization initiator in an aqueous medium. In this case, the face to be printed of the material to be printed 3 is printed in such a way that the face is covered with a single-tier ink layer by making numerous single color ink droplets to adhere to the face, and the monochromatic solid printing process is adopted. Further in this case, when a static contact angle γ_w to pure water on the face to be printed satisfies $\gamma_w 60^\circ$ and an ink volume to be imparted per unit area during printing a monochromatic image solidly is given as VL (pl/cm²) and the ink volume to be absorbed by the face to be printed is given as VR (pl/cm²), the ink and the material to be printed 3 which satisfy conditions $VR \leq VL \times 0.5$ are used to perform the printing process.



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CLAIMS

[Claim(s)]

[Claim 1] In the printing approach of performing ink jet printing to a printed material into an aqueous medium using the ink which contains a pigment, the water-soluble ultraviolet-rays polymerization nature matter, and a water-soluble photopolymerization initiator at least Static contact angle γ to the pure water of this printed side when the case where it prints so that a majority of ink droplets of the ink of one color may be made to adhere to the printed side of a printed material and this printed side may be covered in an one-layer ink layer is considered as 1 color poor printing [Equation 1] $\gamma \leq 60$ degree ... (1)

It is [Equation 2], when it is satisfied, and it 1-color-poor-prints and the volume of the ink in which VL (pl/cm²) and said printed side may absorb the ink volume per [to give] unit area is set to VR (pl/cm²). $VR \leq VL \times 0.5$... (2)

The ink jet printing approach characterized by printing using the ink and the printed material which fill *****.

[Claim 2] In the printing approach which uses aqueous ultraviolet curing mold ink for the printed side of a printed material, and prints by the ink jet method (1) The process which prints by the ink jet method on conditions according to claim 1 to the printed side of a printed material and to print, (2) The process which stiffens the ink which irradiated ultraviolet rays at the printed side after printing in a process (1), and adhered to this printed side, (3) The ink jet printing approach characterized by having the process which removes the solvent component contained in said ink from this printed material after stiffening the ink which is in the printed side of a printed material by said UV irradiation.

[Claim 3] The ink jet printing approach according to claim 1 or 2 that said printed material has the sheet configuration of light transmission nature, and performs said UV irradiation from front flesh-side both sides of the printed material of this sheet configuration.

[Claim 4] The ink jet printing approach according to claim 2 or 3 that removal of the solvent component in a printed material is performed using the dryer equipped with microwave oscillation equipment.

[Claim 5] The ink jet printing approach according to claim 2 or 3 that removal of the solvent component in a printed material is performed by the evaporation desiccation process following backwashing by water of a printed material, and it.

[Claim 6] The ink jet printing approach according to claim 2 or 3 that removal of the solvent component in a printed material is performed by the exposure of far infrared rays.

[Claim 7] The ink jet printing approach according to claim 1 to 6 that said pigment is distributing in said aqueous medium as a particle dispersing element in the range whose mean particle diameter is 25nm - 250nm, and uses together the light source with a wavelength of about 254nm and the light source with a wavelength of about 365nm as the ultraviolet-rays light source.

[Claim 8] The ink jet printing approach according to claim 1 to 7 that an aqueous medium contains a water-soluble ***** solvent.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the printing approach to the printed material in the aqueous ultraviolet curing mold ink which used the ink jet printer. The pigment distributed in more detail by the water soluble dye or the drainage system as a color-material component, The water-soluble polymerization nature compound which carries out a polymerization effectively by the ultraviolet rays as a binder component, The ink jet ink which contains a water-soluble photopolymerization initiator in an aqueous medium is used. printing whose printed material the adhesion force to the printed material of the ink after hardening is high, and is light transmission nature and which was excellent in transparency when becoming — moreover, a printed material is related with the ink jet print processes which are light reflex nature and which will enable high printing of gloss and saturation if it becomes.

[0002]

[Description of the Prior Art] The water color ink which contains a water-soluble color as a color material as ink for ink jets has been used from the former. However, in the water-color-ink independent using water soluble dye, there are many limitations in raising a water resisting property and lightfastness, and the water color ink which uses a pigment is examined instead of being water soluble dye.

[0003] Moreover, in order to obtain a more advanced water resisting property etc., using water pigment ink as an ultraviolet curing mold is performed, for example, the pigment ink of a water ultraviolet curing mold is indicated by JP,7-224241,A.

[0004]

[Problem(s) to be Solved by the Invention] However, when it printed to the common recorded material for ink jets in pigment ink, pigment particles were scattered about on the medium front face, and there was a problem that the transparency of an ink layer and sufficient glossiness may not be acquired. ***** in which the requests to the pigment ink which high printing of transparency is called for and fully fills this demand when it uses for the medium of a light transmission mold which guesses an ink jet technique for lighting from back like OHP, and shows an image brightly especially mounted. Moreover, also in the medium of industrial ways, such as an electric-spectaculars signboard and an electrochromatic display panel, printing which has lightfastness and transparency is called for and the application of ink jet printing using the pigment ink of this field is also being considered.

[0005]

[Problem(s) to be Solved by the Invention] If it prints in a pigment and the ink containing ultraviolet curing mold resin, since the pigment condensation at the time of fixing decreases, the refractive-index difference of resin and a pigment is small and the rate of optical refraction and dispersion will decrease, transparency improves to some extent. However, when this ultraviolet curing mold ink was printed to the recorded material which has sufficient ink absorptivity like the common OHP film for ink jets, it turned out that sufficient effectiveness is not acquired.

[0006] On the other hand, in printing by the water color ink of the ultraviolet curing mold to the medium of non-ink absorptivity, when the wettability to the ink of a medium was bad, the surface tension of ink needed to be reduced. Moreover, it was difficult to obtain a uniform ink layer with high resolution also by such case, and the application of the obtained printed matter had the case where it became what was limited.

[0007] printing whose printed material this invention is made in view of the trouble in the case of using this ultraviolet curing mold ink for printing by the ink jet method, its adhesion force to the printed material of the ink after hardening is high, and is light transmission nature and which was excellent in transparency when becoming — moreover, a printed material sets it as the purpose to offer the gloss and the ink jet print processes which enable high printing of saturation which are light reflex nature, if it becomes.

[0008]

[Means for Solving the Problem] In the printing approach that the ink jet printing approach of this invention performs ink jet printing to a printed material into an aqueous medium using the ink which contains a pigment, the water-soluble ultraviolet-rays polymerization nature matter, and a water-soluble photopolymerization initiator at least Static contact angle γ_{maw} to the pure water of this printed side when the case where it prints so that a majority of ink droplets of the ink of one color may be made to adhere to the printed side of a printed material and this printed side may be covered in an one-layer ink layer is considered as 1 color poor printing [0009]

[Equation 3] $\gamma_{\text{maw}} \leq 60 \text{ degree} \dots (1)$

It is [0010], when it is satisfied, and it 1-color-poor-prints and the volume of the ink in which VL (pl/cm²) and said printed side may absorb the ink volume per [to give] unit area is set to VR (pl/cm²).

[Equation 4] $VR \leq VL \times 0.5 \dots (2)$

It is characterized by printing using the ink and the printed material which fill *****.

[0011] According to this invention, even when the printed material of non-ink absorptivity is used in ink jet printing using

water ultraviolet curing mold ink, the wettability in the printed side of a good printed material can be acquired, and good ink jet printing is attained.

[0012]

[Embodiment of the Invention] If the amount of ink grants in the case of saying printing on the printing conditions which need one ink layer formed using the ink of one color as above-mentioned to be formed so that the whole printed side surface of a printed material may be covered, for example, forming the uniform ink layer of predetermined thickness using the same printed material is calculated by the degree type, "1 Color poor printing" in this invention will become as arranged to the following table 1.

[0013]

[Equation 5] Amount = resolution number x resolution number x of ink 1 dot drop volume / area given to 1 color poor printing (inch square)

[0014]

[Table 1]

表1 (1色べた印刷に付与するインク量VL)

解像度	1ドットの 液滴体積	VL	
		ml/m ²	pl/cm ²
180dpi	200pl	10.0	1.00×10 ⁶
300dpi	120pl	16.7	1.67×10 ⁶
360dpi	80pl	16.0	1.60×10 ⁶
600dpi	40pl	22.3	2.23×10 ⁶
720dpi	35pl	28.1	2.81×10 ⁶

[0015] On the other hand, in order to form the ultraviolet-rays hardened material from ink in the printed side of a printed material in the good condition It is necessary to remain on a printed side, without absorbing sufficient amount of the ink supplied on the printed side of a printed material in a printed material. The value of VR in the case of printing on the conditions in each numeric value of the above-mentioned table 1 (volume of the ink (liquid) which a printed side may absorb) needs to take a value smaller enough than the above-mentioned VL. Then, in this invention, to VL, it is fully small, namely, the combination of the printed material and ink which can offer VR which fills the above-mentioned formula (2) is used. In addition, VL is an amount for which it mainly depends on the resolution of a printer, and the volume of the ink droplet per dot, and it can adjust by changing these conditions as shown in Table 1. In addition, it can judge whether good solid printing is attained by the whole field's being in uniform concentration under a naked eye and a microscope, and not observing a minute particle with the high concentration by condensation of a color-material particle.

[0016] Moreover, VR is the numeric value which changes various magnitude of a liquid ink drop, performs one color - 3 color poor printing to a printed material, can measure as an ink absorbed amount per unit area, and can be acquired from the dryness of the front face of 10 minutes after.

[0017] In addition, the numeric value about the resolution shown in Table 1 and an ink droplet shows the typical conditions in 1 color poor printing, and is not limited to these. Moreover, the conditions of the formula (2) about 1 color poor printing in this invention specify the conditions about the combination of a printed material and ink, and various kinds of print modes are applied according to printed information, such as mixing of printing by the dot, and the poor printing section and dot printing used as printing described to the same field in the ink of two or more colors, and poor printing, in actual printing. For example, when including printing by the dot, it may print so that 1 ink droplet may serve as an amount smaller than the amount shown in Table 1. In that case, although extent of the coalescence between adjoining dots (overlap in a periphery) decreases, in addition, the conditions of a formula (2) are effective as a working condition for acquiring transparency. Moreover, in the usual color picture printing, since the ink of the amount of two or more colors is given to an unit area, the ink of the amount which exceeds clearly the amount of ink grants of 1 color poor printing in fact will be given. Therefore, in printing using the approach of this invention, the ink which the printed material did not absorb the ink whole quantity given inside, and was not absorbed remains in sufficient amount for a front face, and hardening fixing is carried out by ultraviolet rays.

[0018] When using the printed material of light transmission nature for the approach of this invention, it is thought that it is based on the following reasons that sufficient transparency is acquired.

[0019] For example, when the wettability to water color ink is bad or prints to a printed material lacking in absorptivity, it carries out by preparing the acceptance layer which generally has ink absorptivity. However, if there is an acceptance layer which has sufficient ink absorptivity, the phenomenon in which components other than the pigment particle in ink (for example, aqueous medium in the condition that the water-soluble polymerization nature compound etc. was included) permeate into an acceptance layer will happen. Since sufficient amount of a polymerization nature compound does not remain in a front face or its near even if a pigment particle remains in a front face and a water-soluble polymerization nature compound carries out a polymerization by UV irradiation, it stops consequently, achieving the function to which the hardening film by ultraviolet rays wraps a pigment particle, and fixes this. Then, the hardening film particle formed in the front face of a pigment particle will cause light scattering, and does not discover the adhesion force of a pigment particle, either. On the other hand, since ink carries out UV hardening certainly to the timing to which sufficient amount of the water-soluble

polymerization nature compound in ink and a water-soluble polymerization initiator remains in the medium front face with the pigment in filling the relation of the aforementioned (2) formula, it is thought that sufficient transparency, gloss, and adhesion force are obtained.

[0020] On the other hand, the printed material which fulfills the conditions of said formula (2) usually has non-ink absorptivity or low ink absorptivity. The wettability of ink and a base material must be adjusted so that it may be satisfied with printing to such a printed material of the aforementioned (1) formula in addition to the conditions of said formula (2). Although the combination of the ink which fills a formula (1), and a printed material can be attained by adjusting one [these / at least] physical properties, it is desirable to carry out surface treatment of the field where the physical properties of the printed side serve as a printed side of selection or a printed material as a printed material in what fulfills the conditions of a formula (1), and to acquire it.

[0021] By reference, the static contact angle over the pure water in general-purpose plastics is shown in Table 2. In these plastics, the static contact angle over pure water is 70 degrees or more. That is, it can be said that these general-purpose plastics of the wettability to water is low.

[0022]

[Table 2]

表2 (汎用プラスチックの静的接触角)

プラスチック名称	純水の静的接触角 (度)
低密度ポリエチレン	94
ポリ塩化ビニル	87
ポリ塩化ビニリデン	80
ポリテトラフルオロエチレン	108
ポリエチレンテレフタレート	76~81
ポリメチルメタクリレート	80
6-6ナイロン	70~72
ポリスチレン	91

[0023] In order to print from such a thing in the ink which contains water at least on the sheet of plastics, the approach of lowering own surface tension of ink to ink by the approach of adding a surfactant, and the ink on a sheet being damp, and enlarging breadth has been taken. and the solvent of ***** like (2) ethyl alcohol which mixes with water to coincidence the organic solvent which can mix with water like (1) methyl ethyl ketone and gamma PUCHIRO lactone, and has compatibility also in plastics, and is used for it as a solvent component of ink, and isopropyl alcohol — ink — adding — evaporation of the solvent component of the ink on a sheet — base — it advanced quickly, and viscosity was raised and the approach of preventing heterogeneous diffusion was also used together. However, these approaches of the precision of the workmanship were completely insufficient for poor printing which needs a precise image or high homogeneity, even if it could draw the image of the low resolution by big dot which prints a code.

[0024] In this invention, the desirable printing result of high resolution is preferably obtained by obtaining the printed material with which can be satisfied of the relation of (1) type by selection or surface treatment. When aiming at transparent printing to the printed material of light transmission nature, it is the range which does not lose the smooth nature of the front face of a printed material, or it is especially effective to perform surface treatment of a printed material including increasing surface smooth nature.

[0025] If ink and a base material have the relation expressed with the above-mentioned formula (1) and (2), on the printed side of a printed material, breadth and the adjoining drop coalesce effectively and the drop of the ink which flew and reached the target from the nozzle can form a smooth drop layer. If it shifts from this relation, the case where contract, coalesce in both drops and uniform liquid membrane is not formed will produce a drop. Consequently, since it enlarges light scattering very much in not obtaining the smooth feeling as an image, and a feeling of homogeneity and requiring transparency, the case where it is lost produces transparency in practice.

[0026] (1) It is gammao [as opposed to an aqueous liquid to the front face which turns into a printed side of the base material of desired configurations, such as a sheet configuration which can constitute a printed material, as the approach of satisfying a formula]. The method of performing surface treatment is desirable so that it may be made to go up, ink is damp and a flare is guaranteed by this. That is, it is effective to use a water soluble polymer compound with the absorptivity of water color ink, a metallic oxide, etc. in the range of conditions (1).

[0027] (1) As an option to which a formula is satisfied, physical surface treatment, such as vacuum evaporation of oxygen plasma oxidation, an electron beam exposure, the far-ultraviolet-rays exposure of about 200nm, flame (flame) processing, oxidation silicon, oxidation aluminum, etc. and sputtering, is effective.

[0028] In the water color ink of the invention in this application using the matter of ultraviolet-rays hardenability, the printing approach corresponding to two kinds of following ink ingredient configurations and it is employable, for example. As the printing approach, the removal process for a solvent (evaporation, stoving, rinsing) is included.

[0029] The 1st ink ingredient configuration is a constituent which consists of the pigments, the water, the water-soluble

liquefied polymerization nature compounds, and the water-soluble photoinitiators as a color material. Here, since a water-soluble liquefied polymerization nature compound also demonstrates *****, a non-volatile hydrophilic-property solvent which is used in common drainage system ink jet ink is not used. The 2nd ink ingredient configuration is a constituent which consists of the pigment as a color material, water, a water-soluble organic solvent, water-soluble liquefied ultraviolet-rays hardening resin, and a water-soluble photoinitiator.

[0030] Hereafter, each component is explained.

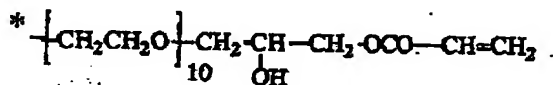
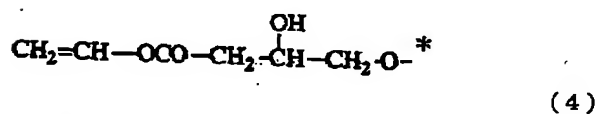
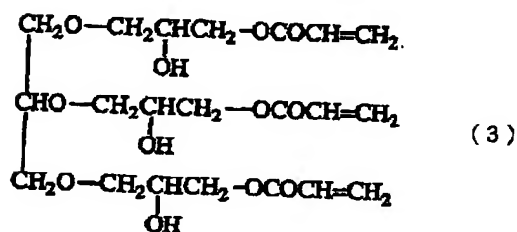
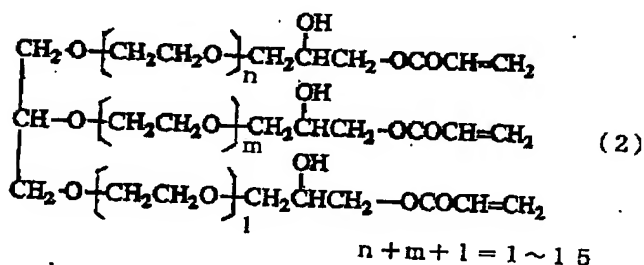
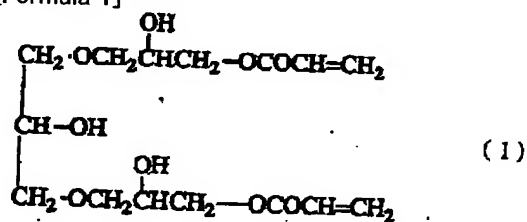
[0031] As water-soluble polymerization nature matter hardened by <water solubility polymerization nature matter hardened by ultraviolet rays> ultraviolet rays, the polymerization nature compound of monofunctional or many organic functions can be used. Also in it, it has two or more acryloyl radicals in 1 molecule, and a compound whose solubility to water is 10 % of the weight or more is desired. And it dissolves in water until now, and viscosity is low, there is photopolymerization nature, and it was known whether the matter excellent also in the physical properties of the hardening film is very few. The compound which has polyethylene-glycol structure among the matter of many organic functions which dissolves in water is the typical matter. However, even if there is water solubility, these have the bad water resisting property of a paint film, and the base material stuck well also has a limit. Although the acrylic ester guided from the epichlorohydrin addition compound of polyhydric alcohol and the compound group generally called epoxy acrylate have high water solubility, and an ultraviolet-rays cure rate is also excellent also in paint film physical properties early, and it has many hydroxyl groups therefore, there is the description that viscosity is a little high. For this reason, use in ink may be restricted.

[0032] The shape of liquid is presented, hygroscopicity is high at a hydrophilic property and the thing which do not contain a non-volatile organic solvent and for which the aqueous ink jet ink of the 1st configuration is constituted becomes possible by using the ultraviolet-rays polymerization nature compound of a non-volatile.

[0033] One of the polyfunctional polymerization nature compounds is acrylic (meta) ester of polyhydric alcohol. As a compound water-soluble into this group, polyethylene-glycol #200 diacrylate, polyethylene-glycol #200 diacrylate, etc. which are acrylic ester of a polyethylene glycol are mentioned. Furthermore, the water-soluble epoxy acrylate represented by the following compounds can also be used.

[0034]

[Formula 1]



**** can be mentioned.

[0035] Acrylic ester of the polyol which can also use the polymerization nature compound which has the water solubility of the Nonion nature, and has two or more hydroxyl groups, such as monosaccharide and two saccharides, as such a

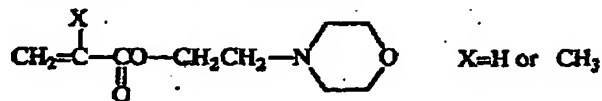
polymerization nature compound (meta); acrylic ester (meta), such as triethanolamine, diethanolamine, tris hydroxy aminomethane, and tris hydroxy aminoethane, can be mentioned. These have some fundamental elements of this invention called water solubility and polymerization nature, and are desirable compounds.

[0036] The acrylate of the following structure is high reactivity, and since it is hypoviscosity, it is especially used preferably as a component of the ink in this invention.

[0037]

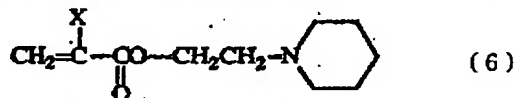
[Formula 2]

morpholinoethyl(meth)acrylate



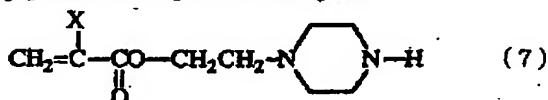
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piperidinoethyl(meth)acrylate



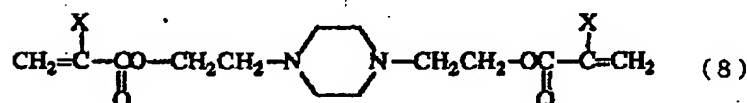
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piperadinoethyl(meth)acrylate



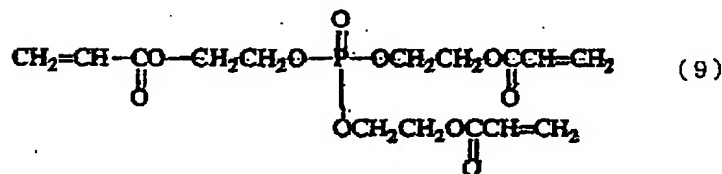
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N,N'-di-[(meth)acryloyl ethyl] piperadine



(8)

tris(acryloyl oxo ethoxy) phosphate



(9)

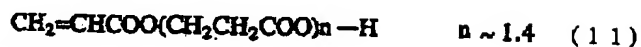
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[Formula 3]

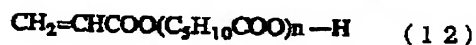
β -acryloyloxyethylhydrogensuccinate



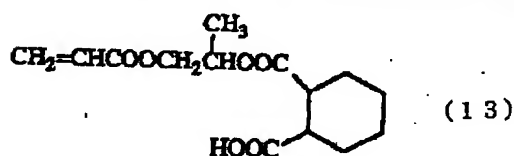
carboxyethylacrylate



w-carboxypolycaprolactone monoacrylate

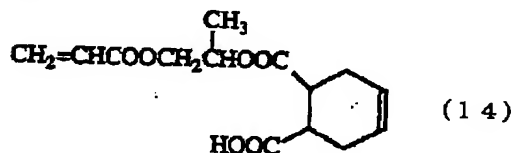


2-acryloyloxypropyl hexahydro hydrogen phthalate



[化 11]

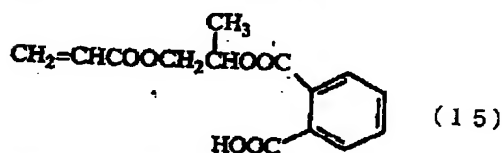
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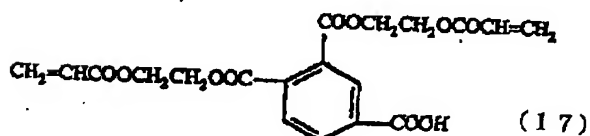
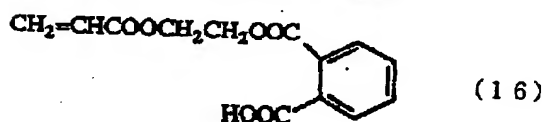
[0039]

[Formula 4]

2-acryloyloxypropyl hydrogen phthalate



2-acryloyloxyethyl hydrogen phthalate



[0040] Formula (5) Hypoviscosity, high reactivity, and each water-soluble demand are filled, use of oligomer with high viscosity becomes easy by many organic functions, and each compound of - (17) can raise the content of the active substance in ink by it.

[0041] The content in the inside of the ink of these polymerization nature compounds is the amount of 5 times of the content of color material, tales doses, or the content of color material preferably one to 40% of the weight. That is, if color material is 3 % of the weight, it is desirable to consider as 3 - 15 % of the weight.

[0042] Including the polymerization nature compound which also has a function as the above-mentioned solvent, in order to make photopolymerization perform to this polymerization nature compound, a water-soluble photopolymerization initiator is used together by the ink used by <photopolymerization initiator> this invention. As this water-soluble (hydrophilic property) photopolymerization initiator, the water-soluble photopolymerization initiator of the quarternary-ammonium-salt mold shown below can be used.

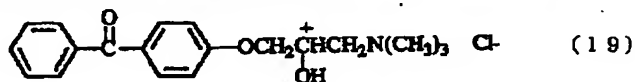
[0043]

[Formula 5]

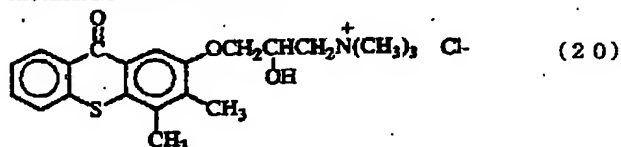
[4-benzoyl-N,N,N-trimethyl benzene methane ammonium chloride]



[2-hydroxy 3-(4-benzoyl-phenoxy)-N,N,N-trimethyl 1-propane ammonium chloride]



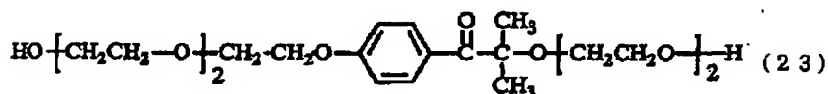
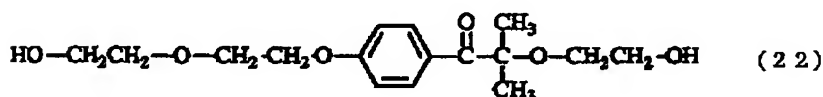
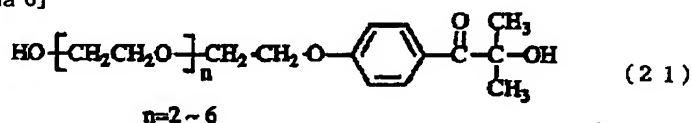
[4-benzoyl-N,N dimethyl N-[2-(1-hydroxy-2-propenyloxy) ethyl] benzene methammonium bromide]



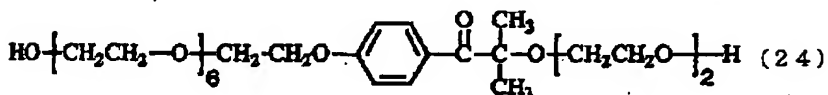
[0044] Since these compounds are quarternary-ammonium-salt structures, they have high water solubility.

[0045]

[Formula 6]



[化 2 6]



[0046] Formula (21) Since the compound of - (24) does not have a dissociative radical, it is an especially desirable compound in the semantics that a problem cannot arise in ***** with color material easily.

[0047] The content in the inside of the ink of a photopolymerization initiator can be preferably made into 0.3 - 3 % of the weight 0.1 to 10% of the weight.

[0048] As for the pigment as a color material used for the ink used in <pigment> this invention, it is indispensable that it is that by which the distributed condition in a particle is stabilized and is maintained in the liquid medium. In this invention, an aqueous medium distributes, and a fundamental element has the particle size distribution as a dispersing element in the range of 25nm - 250nm with mean particle diameter, and are [that it can adjust in the range which does not affect the regurgitation / the viscosity of the last ink /, and / of compatibility ** with an indispensable component] satisfied with ultraviolet-rays hardenability.

[0049] In order to obtain such a pigment dispersing element, the approach using the polymer dispersant indicated by JP,10-168151,A etc. as a base material etc. is suitable. Moreover, the surfactant indicated by JP,8-209048,A etc. is also suitable.

[0050] The most important business is in <printing condition> this application to carry out so that the formula (1) which mentioned the relation between a printing base material and ink previously, and the relation of (2) may be satisfied. ink which expresses these conditions qualitatively and which will have been conventionally performed by the ink jet method if it becomes — base — moreover, it does not mean quickly preparing the printed material which may fully be absorbed. It becomes requirements required for an essential target in order to make the target printing attain in this invention not to give such absorptivity. This invention has the description at the point that the amount of ink which a printed material may absorb is controlled, rather than the ink total amount given by 1 color poor printing.

[0051] In order to obtain a transparent printing result substantially using aqueous ultraviolet curing ink as a result of various experimental examination, it is required to print by satisfying the relation of the above-mentioned formula (1). If the following means are taken, it is easy to be referred to as one half of the ink total amounts of 1 ***** to which the amount of ink which a printed material may absorb is given, as stated previously. Although the wettability to water color ink is good, however surface treatment by which the osmosis absorbed amount is controlled was made or wettability is good in order to satisfy such conditions, permeability should just prepare the base material which it does not have at all.

[0052] Here, the ingredient approach of performing surface treatment by which the osmosis absorbed amount is controlled is

shown. Desirable surface treatment material is hydrophilic resin for coatings. They are polyvinyl alcohol, water polyurethane, aqueous polyester, a polyvinyl acetal, the polyethylene oxide over which the bridge was constructed, the water-soluble polyamide over which the bridge was constructed, the polyamide of alcoholic fusibility, the melamine resin of a hydrophilic property, acrylic resin of a hydrophilic property, etc. As for these resin, using as those bridge formation objects is desirable the moisture resistance of printed matter, and in respect of a water resisting property. Aldehydes, melamines, poly epoxide, block isocyanate, and aluminum alkoxides are used for bridge formation. Although such surface treatment has fixed ink absorptance, it cannot have quick rate of absorption.

[0053] Since the ink absorbed amount of a printed material is controlled and the ink hardening method (ultraviolet curing method) by UV irradiation is further used by the printing approach of this application, the ink rate of absorption of a printed material becomes almost essential less. Therefore, almost all the approaches learned as a surface treatment method to the hydrophilic side of a metal or the predetermined side of plastics can apply fundamentally. For example, inorganic coating of applying noble metals, such as the gold and silver which apply metallic oxides, such as a silica, an alumina, and a magnesia, from a gaseous phase, and copper, is also effective in doubling the wettability to a front face. If the conditions of a formula (1) are satisfied and an ultraviolet curing method is adopted, pigment ink printing will be attained for printing excellent in the transparency in a penetrable base material, the saturation in a reflective mold base material, concentration, and lightness.

[0054] The aqueous medium used in <solvent> this invention could be formed by the water independent as mentioned above, if needed, mixed the water-soluble organic solvent in water, and could be formed in it. In using a water-soluble organic solvent, the desiccation process after printing becomes more effective. As a water-soluble organic solvent of the property in which evaporation desiccation is made comparatively easily, the boiling point under atmospheric pressure is the water-soluble organic solvent which is 190 degrees C or less in general. As those examples, ethylene glycol, a diethylene glycol, Triethylene glycol, tripropylene glycol, a glycerol, 1, 2, 4-butane triol, 1 and 2, 6 hexane triol, 1 and 2, 5 pentanetriol, 1, 2-butanediol, 1,3-butanediol, 1,4-butanediol, Dimethyl sulfoxide, diacetone alcohol, glycerol monoallyl ether, Propylene glycol, a butylene glycol, a polyethylene glycol 300, thiodiglycol, A N-methyl-2-pyrrolidone, 2-pyrrolidone, gamma-butyrolactone, 1,3-dimethyl-2-imidazolidinone, sulfolane, a TORIMECHI rule propane, Trimethylethane, neopentyl glycol, ethylene glycol monomethyl ether, Ethylene glycol monoethyl ether, ethylene glycol mono-isopropyl ether, Ethylene glycol monoallyl ether, the diethylene-glycol monomethyl ether, Diethylene glycol monoethyl ether, the TORIECHIRENGURIKORI monomethyl ether, It is triethylene glycol mono-ether, propylene-glycol-monomethyl-ether, dipropylene-glycol-monomethyl-ether, beta-dihydroxyethyl urea, urea, acetonylacetone, pentaerythritol, 1, and 4-cyclohexa diol etc.

[0055] As for the non-volatile solvent with difficult evaporation desiccation, it is desirable to remove by backwashing by water after printing etc. As a solvent which can be used when using such a process Moreover, hexylene glycol, the ethylene glycol monopropyl ether, Ethylene glycol monobutyl ether, the ethylene glycol mono-isobutyl ether, Ethylene glycol monophenyl ether, diethylene-glycol diethylether, The diethylene-glycol monobutyl ether, the diethylene-glycol mono-isobutyl ether, Triethylene glycol monobutyl TETERU, triethylene glycol wood ether, Triethylene glycol diethylether, tetraethylene glycol wood ether, Tetraethylene glycol diethylether, the propylene glycol monobutyl ether, Dipropylene glycol monomethyl ether, the dipropylene glycol monopropyl ether, The dipropylene glycol monobutyl ether, tripropylene glycol monomethyl ether, Glycerol monoacetate, buri serine diacetate, triacetin, Ethylene glycol monomethyl ether acetate, diethylene-glycol monomethyl ether acetate, A cyclohexanol, 1, 2-cyclohexane diol, 1-butanol, It is 3-methyl -1, 5-PENTA diol, 3-hexene -2, 5-diol, 2, 3-butanediol, 1,5-pentanediol, 2, 4-pentanediol, 2, and 5-hexandiol etc.

[0056] In this invention, when they are added with the high content since polymerization nature oligomer possesses the evaporation tightness ability of the water as a solvent as previously mentioned as the 1st configuration, the configuration which does not use the above-mentioned solvents as a solvent is also possible. When using solvents, the total amount of a water soluble solvent is 5 - 40 % of the weight to the whole ink in general. In addition, a water soluble solvent can combine and use the two or more sorts within limits which do not spoil the effectiveness of this invention.

[0057] <Color ink> The color ink in the case of next using for color record is explained. As a color material of color ink, an organic pigment, for example, the pigment dispersing element distributed with the dispersant, is applicable. Moreover, it uses [with a pigment] well-known direct dye, acid dye, reactive dye and those metal complexes, polyvalent metallic salt, etc. together and is conventionally usable. However, since ultraviolet rays are irradiated after record, a stable color and an organic pigment are desirable to light.

[0058] As an organic pigment which has a hue as a process color used for <pigment> color ink As a yellow pigment The pigment yellow 1, 2, 3, and 12, the pigment yellow 13, the pigment yellow 14, the pigment yellow 16, the pigment yellow 17, the pigment yellow 55, the pigment yellow 73, the pigment yellow 74, the pigment yellow 75, the pigment yellow 83, the pigment yellow 93, and a pigment yellow — 95, the pigment yellow 97, the pigment yellow 98, the pigment yellow 109, the pigment yellow 110, the pigment yellow 114, and the pigment yellow 128 — They are the pigment yellow 138, the pigment yellow 139, the pigment yellow 150, the pigment yellow 151, the pigment yellow 154, the pigment yellow 180, etc.

[0059] As a Magenta pigment, the pigment red 5, the pigment red 7, a pigment 12, a pigment 48 (calcium), the pigment red 48 (Mn), the pigment red 57:1, the pigment red 57 (Sr), the pig noodle trend 57:2, the pigment red 122, the pigment red 123, the pigment red 168, a pigment 184, the pigment red 202, the pigment red 238, etc. are applied.

[0060] As a cyanogen pigment, the pigment blue 1, the pigment blue 2, the pigment blue 3, the pigment blue 16, the pigment blue 22, the pigment blue 60, the pigment blue 15:2, a pigment 15:3, the putt blue 1, the putt blue 60, etc. are applied.

[0061] This application makes the theme fundamentally achievement of the transparency in particle pigment ink, and adhesion force. However, use of a color is not barred, and also when a color is used, desirable effectiveness is brought about in addition to some fading by ultraviolet rays. That is, they are saturation, concentration, and lightness.

[0062] Fundamentally, although a color is weak, by choosing the wavelength and reinforcement of the light used for ultraviolet curing, lightfastness can be suppressed to the minimum and it can apply the fading substantially in many cases. The following can be mentioned as a color which can be used together with a pigment.

[0063] As a yellow color The ASSHIDO yellow 11, the ASSHIDO yellow 17, the ASSHIDO yellow 23, the ASSHIDO yellow 23, the ASSHIDO yellow 25, the ASSHIDO yellow 29, the ASSHIDO yellow 42, the ASSHIDO yellow 49, the ASSHIDO yellow 61,

the ASSHIDO yellow 71, The direct yellow 12, the direct yellow 24, the direct yellow 26, the direct yellow 44, the direct yellow 86, the direct yellow 87, the direct yellow 98, the direct yellow 100, the direct yellow 130, They are the direct yellow 86, the direct yellow 132, the direct yellow 142, etc.

[0064] As a Magenta (red) color The ashy dreadlocks 1, the ashy dreadlocks 6, the ashy dreadlocks 8, the ashy dreadlocks 32, the ashy dreadlocks 35, the ashy dreadlocks 37, the ashy dreadlocks 51, the ashy dreadlocks 52, the ashy dreadlocks 80, the ashy dreadlocks 85, the ashy dreadlocks 87, the ashy dreadlocks 92, The ashy dreadlocks 94, the ashy dreadlocks 115, the ashy dreadlocks 180, the ashy dreadlocks 254, the ashy dreadlocks 256, the ashy dreadlocks 289, the ashy dreadlocks 315, the ashy dreadlocks 317, the direct red 1, the direct red 4, the direct red 13, The direct red 17, the direct red 23, the direct red 28, the direct red 31, the direct red 62, the direct red 79, the direct red 81, the direct red 89, the direct red 227, the direct red 240, The direct red 242, the direct red 243, etc. are applicable.

[0065] As a cyanogen color The ASSHIDO blue 9, the ASSHIDO blue 22, the ASSHIDO blue 40, the ASSHIDO blue 59, the ASSHIDO blue 93, the ASSHIDO blue 102, the ASSHIDO blue 104, the ASSHIDO blue 113, the ASSHIDO blue 117, the ASSHIDO blue 120, the ASSHIDO blue 167, The ASSHIDO blue 229, the ASSHIDO blue 234, the ASSHIDO blue 254, direct blue 6, the direct blue 22, the direct blue 25, the direct blue 71, the direct blue 78, the direct blue 86, the direct blue 90, the direct blue 106, The direct blue 199 etc. is applicable.

[0066] If a hue, lightfastness, and solubility are satisfied not only such existing color material but in the compound developed newly, in the configuration of this invention, it is applicable without big difficulty.

[0067] As for the weight as a pure part of the pigment of the pigment in ink, it is desirable to consider as 0.5 thru/or 10.0 % of the weight. Moreover, when using a color together, it is desirable to consider as 0.1 - 5 % of the weight.

[0068] Conventionally [<particle diameter of pigment in ink>], if the particle diameter of a pigment is made into about 0.2 microns or less in use of ink, a coating, and the pigment to plastics, it will have been said that transparency begins to improve very much. However, a result with very bad transparency may be brought in the common ink jet pigment ink which made mean particle diameter 0.2 microns or less. On the other hand, according to the approach of this invention, in addition to the transparency based on the particle diameter of a pigment, the transparency which was excellent with hardening of an ultraviolet-rays polymerization nature compound is discovered. Therefore, if the print processes of this invention are taken, the mean particle diameter of a pigment particle should be just contained in the range of 25nm - about 250nm. Although it depends for this range also on the application of printed matter, in general semantics, the printed matter which can fully be said to be transparency is given. Of course, although the small thing of pigment grain size is desirable, whenever it uses the approach of this invention, it will not be necessary to set particle diameter to 100nm or less.

[0069] Although the <creation approach of ink> ink may mix the raw material to be used in what kind of sequence, mixing is performed without holding an uneven condition for a long time promptly. Moreover, in using a pigment dispersing element, it still more often stirs so that homogeneity may not be spoiled.

[0070] In the print system which carries out <printer system> this invention, a black light is required for an ink jet device. A black light is arranged in a location which is typically illustrated by drawing 1 . Ultraviolet rays are irradiated by the recording paper which came out of the print station from both the upper part, the lower part, or the upper and lower sides. In the case of a transparent base material, of course, such selection is possible. Best is carried out in the time amount region which is maintaining the condition that the time interval from a print head to exposure area has the ink component before ink permeates the recording paper completely in homogeneity. On the printing conditions of this invention that the infiltration capacity force of a base material was controlled in the semantics, the permission width of face of the timing is large. Even if there are many classes of record base material, since the osmosis is controlled, it will become possible to ensure a hardening-exposure.

[0071] A <UV irradiation lamp> UV irradiation lamp has the desirable mercury-vapor lamp with which the vapor pressure of mercury was lit with the mercury-vapor lamp etc. and the so-called low-pressure mercury lamp which is 1-10Pa, the high-pressure mercury lamp, and the fluorescent substance were applied. The range of the emission spectrum of the ultraviolet-rays field of these mercury lamps is 184 to 450nm, and it is suitable for making the matter of black or the polymerization nature in the colored ink react efficiently. Moreover, since a small power source can be used also when a power source is carried in a printer, it is suitable also in the semantics. Since a metal hide lamp, a high-pressure mercury-vapor lamp, an ultrahigh pressure mercury lamp, a xenon flash lamp, a deep UV lamp, UV laser, etc. are used for the mercury lamp and the above-mentioned range is included as a luminescence wavelength field, it is fundamentally applicable if the shape of power-source size, input reinforcement, and ramp type etc. is allowed. The light source is chosen also according to the sensibility of the catalyst to be used.

[0072] Required ultraviolet-rays reinforcement has desirable extent of 2 - 50 mW/cm² from the location of a rate of polymerization. The adhesion force to the recording paper of the ink which fixed when addition exposures were insufficient does not fully come out. Moreover, in color record, lack will arise in the robustness of printing ink which is the purpose of this invention of a water resisting property fully not coming out.

[0073] As for the print processes of <presswork> this invention, it is desirable to have the following processes fundamentally. (1) the process which removes the solvent component in the process (3) base material which irradiates ultraviolet rays and carries out the polymerization of the polymerization nature matter in ink to the process (2) base material printed with an ink jet printer to a base material — a process (3) may be before (2) or may be the back here.

[0074] In this invention, the ink competence of an ink absorbing layer is not enough, and since the solvent remains near the front face, in order to remove a non-evaporated solvent component, it is desirable to use the process of (3).

[0075] However, as stated previously, when using an volatile high organic solvent comparatively by water solubility, or when not using a water-soluble organic solvent, there is not a process of (3). The heating approaches, such as microwave oscillation equipment and a far-infrared lamp, are employable as removal of a solvent component. Moreover, if it is the base material with which it has resistance to water after ultraviolet curing when using the solvent of a non-volatile, rinsing is simple and most effective.

[0076] By making ink fix by ultraviolet rays, good fixing, scratch nature, a water resisting property, etc. are obtained.

Deformation of curl of the form itself, a cockle, etc. is controlled with it, and it is dealt with, and will become desirable also for preservation.

[0077] An example explains still more concretely below. Measurement of mean particle diameter is the numeric value performed by dynamic light scattering.

The example 1 (ink set 1: ink which does not contain a water-soluble organic solvent) of an ink formula

[0078]

[Table 3]

表3 (イエローインク 1)

成分	組成 (重量%)
顔料分散液 [*] (濃度 18%) 顔料分	3.5
水	15.9
水溶性重合性物質「式(17)」	4.0
水溶性重合性物質「式(6)」	13.0
水溶性光重合開始剤「式(21): n=4」	0.5
水	63.1

*) — pigment yellow 74 dispersing element; — mean-particle-diameter: — 110nm and the polyurethane resin (number average molecular weight 3000) of dispersant:water solubility

[0079]

[Table 4]

表4 (マゼンタインク 1)

成分	組成 (重量%)
顔料分散液 [*] (濃度 14%) 顔料分	2.5
水	15.3
水溶性重合性物質「式(17)」	4.0
水溶性重合性物質「式(6)」	13.0
水溶性光重合開始剤「式(21): n=4」	0.5
水	64.7

*) — pigment red 122 dispersing element; — mean-particle-diameter: — 90nm and the polyurethane resin (number average molecular weight 3000) of dispersant:water solubility

[0080]

[Table 5]

表5 (シアンインク 1)

成分	組成 (重量%)
顔料分散液 [*] (濃度 15%) 顔料分	3.0
水	17.0
水溶性重合性物質「式(17)」	4.0
水溶性重合性物質「式(6)」	13.0
水溶性光重合開始剤「式(21): n=4」	0.5
水	62.5

*) — pigment blue 15:3 dispersing element; — mean-particle-diameter: — the polyurethane resin (number average molecular weight 3000) of 75nm, and dispersant:dissolved water in fuel

[0081]

[Table 6]

表6 (ブラックインク 1)

成分	組成 (重量%)
顔料分散液 [*] (濃度 20%) 顔料分	5.0
水	20.0
水溶性重合性物質「式(17)」	4.0
水溶性重合性物質「式(6)」	13.0
水溶性光重合開始剤「式(21): n=4」	0.5
水	57.5

* — pigment black 7 dispersing element; — mean-particle-diameter: — the polyurethane resin (number average molecular weight 3000) of 95nm and dispersant: dissolved water in fuel

The example 2 (ink set 2: ink containing a water-soluble organic solvent) of an ink formula [0082]

[Table 7]

表7 (イエローインク 2)

成分	組成 (重量%)
顔料分散液 (濃度 15%) 顔料分	3.0
水	17.0
水溶性紫外線重合性オリゴマー「式(8)」	4.0
水溶性紫外線重合性オリゴマー「式(7)」	8.0
水溶性光重合開始剤「式(22)」	0.5
水溶性溶剤 2-ピロリドン	10
ジエチレングリコール	5
水	52.5

* — pigment yellow 93 dispersing element; — mean-particle-diameter: — 135nm; dispersant: — the acrylic resin (number average molecular weight 5300) of alkali fusibility

[0083]

[Table 8]

表8 (マゼンタインク 2)

成分	組成 (重量%)
顔料分散液 (濃度 15%) 顔料分	3.5
水	19.8
水溶性紫外線重合性オリゴマー「式(8)」	4.0
水溶性紫外線重合性オリゴマー「式(7)」	8.0
水溶性光重合開始剤「式(22)」	0.5
水溶性溶剤 2-ピロリドン	10
ジエチレングリコール	5
水	49.2

* — permanent Carmine (Permanent Carmine) GG-2105 (pigment red 238) dispersing element; — mean-particle-diameter: — 115nm [0084]

[Table 9]

表 9 (シアンインク 2)

成分	組成 (重量%)
顔料分散液 (濃度 15%) 顔料分	2.5
水	14.2
水溶性紫外線重合性オリゴマー「式(8)」	4.0
水溶性紫外線重合性オリゴマー「式(7)」	8.0
水溶性光重合開始剤「式(22)」	0.5
水溶性溶剤 2-ピロリドン	10
ジエチレングリコール	5
水	55.8

*) — pigment blue 15:3 dispersing element; — mean-particle-diameter: — 75nm; dispersant: — the acrylic resin (number average molecular weight 5300) of alkali fusibility

[0085]

[Table 10]

表 10 (ブラックインク 2)

成分	組成 (重量%)
顔料分散液 (濃度 19%) 顔料分	5.0
水	21.3
水溶性紫外線重合性オリゴマー「式(8)」	4.0
水溶性紫外線重合性オリゴマー「式(7)」	8.0
水溶性光重合開始剤「式(22)」	0.5
水溶性溶剤 2-ピロリドン	10
ジエチレングリコール	5
水	46.2

*) — pigment black 7 dispersing element; — mean-particle-diameter: — 95nm; dispersant: — the acrylic resin (number average molecular weight 5300) of alkali fusibility

The example 3 (ink set 3: ink containing a water-soluble organic solvent) of an ink formula

[0086]

[Table 11]

表 11 (イエローインク 3)

成分	組成 (重量%)
顔料分散液 (濃度 15%) 顔料分	3.0
水	17.0
水溶性紫外線重合性オリゴマー「式(8)」	5.0
水溶性紫外線重合性オリゴマー「式(5)」	7.0
水溶性光重合開始剤「式(19)」	0.5
水溶性溶剤 2-ピロリドン	10
ジエチレングリコール	5
水	52.5

*) — pigment yellow 128 dispersing element; — mean-particle-diameter: — 123nm; dispersant: — phosphor Norian RE610 (HLB=12.6, Toho Chemical make)

[0087]

[Table 12]

表 1 2 (マゼンタインク 3)

成分	組成 (重量%)
顔料分散液 (濃度 15%) 顔料分	3.5
水	19.8
水溶性紫外線重合性オリゴマー「式(8)」	5.0
水溶性紫外線重合性オリゴマー「式(5)」	7.0
水溶性光重合開始剤「式(19)」	0.5
水溶性溶剤 2-ピロリドン	10
ジエチレングリコール	5
水	49.2

*) — pigment red 122 dispersing element; — mean-particle-diameter: — 140nm; dispersant: — phosphor Norian RE610 (HLB=12.6, Toho Chemical make)

[0088]

[Table 13]

表 1 3 (シアンインク 3)

成分	組成 (重量%)
顔料分散液 (濃度 15%) 顔料分	2.5
水	14.2
水溶性紫外線重合性オリゴマー「式(8)」	5.0
水溶性紫外線重合性オリゴマー「式(5)」	7.0
水溶性光重合開始剤「式(19)」	0.5
水溶性溶剤 2-ピロリドン	10
ジエチレングリコール	5
水	55.8

*) — pigment blue 15:3 dispersing element; — mean-particle-diameter: — 110nm; dispersant: — phosphor Norian RE610 (HLB=12.6, Toho Chemical make)

[0089]

[Table 14]

表 1 4 (ブラックインク 3)

成分	組成 (重量%)
顔料分散液 (濃度 19%) 顔料分	5.0
水	21.3
水溶性紫外線重合性オリゴマー「式(8)」	5.0
水溶性紫外線重合性オリゴマー「式(5)」	7.0
水溶性光重合開始剤「式(19)」	0.5
水溶性溶剤 2-ピロリドン	10
ジエチレングリコール	5
水	46.2

*) — pigment black 7 dispersing element; — mean-particle-diameter: — 95nm; dispersant: — phosphor Norian RE610 (HLB=12.6, Toho Chemical make)

[0090] TOREJIN which the polyethylene terephthalate film of 175 microns of examples is used as a base material, and is cross-linking water solubility polyamide resin at this Para toluenesulfonic acid was added to FS500 (water dispersion made from imperial chemistry industry) as a cross linking agent (the water-dispersion 100 section: cross linking agent =100:2

(weight section)), and it applied in wire bar coater #10, and dried at 20 degrees C for 15 minutes. The printed material 1 which has the hydrophilic polyamide resin layer of 4 microns of thickness by this was prepared. The contact angle over the pure water on this front face of a film was 30 degrees. The amount of ink which this film may absorb was 1×10^5 pl/cm² (=1 ml/m²) about as a result of the printing trial. The paint film showed the good water resisting property.

[0091] The printing trial was performed to the ink jet printer of the arrangement configuration shown in drawing 1 using the equipment carrying a UV irradiation lamp. In this testing device, the amount of ink given in 1 color poor printing was set up with 2.2×10^6 pl/cm² using the print head of Bubble Jet. the carried lamp — the product made from the USHIO electrical and electric equipment — it is low-pressure mercury lamp UL1-5DQ (inputs 50W, 90V, and 0.6A). The time amount from which time amount after ink is given until it goes into a UV irradiation field has received UV irradiation for 7 seconds about is 10 seconds about.

[0092] The ink set 1 was used, the pattern which one color (YMC) of colors stated to the printed material 1 was printed, respectively, and UV irradiation was performed. The obtained printed matter carried out evaporation desiccation within microwave irradiation equipment, and obtained desired printed matter. Transparency spectrum measurement was performed using these printed matter. In addition, it printed like the above, without performing surface treatment to the base material in the example 1 of printed material manufacture as a comparison, the printing object was created, and the transparency spectrum was measured. The above measurement result was indicated to Table 15.

[0093] Desirable transparency's being shown is set to 1 in permeability in the wavelength field which becomes 0 in the wavelength region which the color material itself should absorb, and is not absorbed.

[0094]

[Table 15]

表 15 (透過スペクトル測定結果)

	Y		M		C	
	吸収域	透過域	吸収域	透過域	吸収域	透過域
波長 (nm)	400	600	550	650	650	480
透過率 (表面処理あり)	0.03	0.95	0.1	0.97	0.1	0.95
透過率 (表面処理なし)	0.15	0.70	0.25	0.65	0.20	0.55

[0095] In addition, since coalescence of a liquid ink drop did not progress and smooth liquid membrane was not formed, when he had no surface treatment, in order to have evaluated permeability, the homogeneity of printed matter itself was in the very imperfect condition.

[0096] The polyethylene terephthalate film of 275 microns of examples was used as the base material, the mixture (polyethylene glycol: glyoxal =, 100:3 (weight section)) of polyethylene-glycol resin (molecular weight 80,000) and glyoxal was applied to this in wire bar coater #20, and it dried by 125-degree Centigrade for 20 minutes. The printed material 2 which has the polyethylene-glycol resin layer of 10 microns of thickness by this was prepared. This resin front face was a front face which has a water resisting property according to bridge formation, and the contact angle over pure water was 15 degrees. Moreover, the amount of ink which may be absorbed was 4×10^6 pl/cm².

[0097] Using the ink set 2 and the printed material 2, one color (YMC) of a color carried out poor pattern printing like the example 1, and UV irradiation was performed. The obtained printed matter carried out evaporation desiccation with the far-infrared dryer, and obtained desired printed matter. Furthermore, printed matter was obtained by same actuation using the base material (with no surface treatment). Transparency spectrum measurement was performed using these printed matter, and the result was indicated to Table 16.

[0098]

[Table 16]

表 1 6 (透過スペクトル測定結果)

	Y		M		C	
	吸収域	透過域	吸収域	透過域	吸収域	透過域
波長 (nm)	400	600	550	650	650	480
透過率 (表面処理あり)	0.05	0.92	0.08	0.94	0.08	0.94
透過率 (表面処理なし)	0.17	0.82	0.23	0.70	0.22	0.80

[0099] In addition, since coalescence of a liquid ink drop did not progress and smooth liquid membrane was not formed, when he had no surface treatment, in order to have evaluated permeability, the homogeneity of printed matter itself was in the very imperfect condition.

[0100] By using the 7059 glass plates of the thickness of 31.1mm of examples as a base material, the front face was irradiated under the ultraviolet disinfection lamp for 5 minutes, subsequently it cleaned ultrasonically with the alkaline cleaning agent, rinsing desiccation was carried out after that, and the printed material was obtained. The contact angle over the pure water of the surface treatment section of this printed material was 13 degrees. It printed at the following processes using this printed material.

[0101] The bubble jet airline printer arranged so that it can print to the base material on a plate without pliability as shown in drawing 2 and UV irradiation can be carried out from the upper and lower sides of a base material was prepared. The 254nm light source has been arranged in the upper part, and the 365nm light source has been arranged in the lower part. The printing trial was performed to the base material 3 using the ink of the example 3 of a formula using this. The carried lamp sets the upper and lower sides near the main wavelength, and is 5 mW/cm². It is the high pressure mercury vapor lamp which has output characteristics. The ink of the ink set 3 was used respectively, the pattern which one color (YMC) of colors stated to the printed material 3 was printed, and UV irradiation was performed.

[0102] After rinsing the obtained printed matter (colored-glass plate), evaporation desiccation of it was carried out within microwave irradiation equipment. In this way, transparency spectrum measurement was performed using the obtained colored-glass plate. These results were indicated to Table 17.

[0103]

[Table 17]

表 1 7 (透過率スペクトル測定結果)

	Y		M		C	
	吸収域	透過域	吸収域	透過域	吸収域	透過域
波長 (nm)	400	600	550	650	650	480
透過率	0.05	0.96	0.09	0.95	0.7	0.95

[0104] The ethylene terephthalate film of 475 microns of examples was used as the base material, the hoe zinc fluoride hydrochloride was added to this as DENAKORU EX314 which is water-soluble poly epoxide as a cross linking agent of polyvinyl alcohol resin (whenever [molecular-weight by POPARU Kuraray 50,000 saponification] 85%), and a crosslinking reaction catalyst (DENAKORU EX314:hoe zinc-fluoride hydrochloride: 100:5 (weight section)), and it applied in wire bar coater #30, and dried by 120-degree Centigrade for 15 minutes. The printed material 4 which has the polyvinyl-alcohol-resin layer of 10 microns of thickness by this was prepared. The contact angle over the pure water on this front face of a film was 25 degrees. The amount of ink which this film may absorb was 1x10⁶ pl/cm² (=10 ml/m²) about as a result of the printing trial. The paint film showed the good water resisting property.

[0105] The printing trial was performed like the example 1 using the equipment of a configuration of having been shown in drawing 1. The used ink is the ink set 2. Printing and UV irradiation were performed like the example 1. The obtained printed matter carried out evaporation desiccation within hot blast oven, and obtained desired printed matter. Transparency spectrum measurement was performed using these printed matter. The above measurement result was indicated to Table 18.

[0106]

[Table 18]

表 18 (透過スペクトル測定結果)

	Y		M		C	
	吸収域	透過域	吸収域	透過域	吸収域	透過域
波長 (nm)	400	600	550	650	650	480
透過率	0.03	0.95	0.1	0.97	0.1	0.95

[0107] Pie RONARU (Toyobo make) which is hydrophilic polyester resin was applied to the resin coat paper which carried out the laminating of the polyethylene layer to the example 5 base-paper front face in wire bar coater #30, it dried at 120 degrees C for 15 minutes, and the printed material 5 was obtained. In addition, the thickness of a polyester resin layer was 13 micrometers of thickness. The contact angle over the pure water on this front face of the recording paper was 60 degrees. Moreover, the amount of ink which the recording paper may absorb was 0.5×10^6 pl/cm² (=5 ml/m²) about as a result of the printing trial.

[0108] The same equipment as an example 1 was used and the poor pattern of seven colors of YMCKRGB was printed using the ink set 3 and the printed material 5. The obtained printed matter was fed into the heating furnace for 3 minutes, and performed evaporation desiccation. Image concentration and color measurement (saturation, lightness, hue) were performed using these printed matter. Moreover, the image section was ground against the commercial yellow marker, and resistance was evaluated. Consequently, the high scratch nature engine performance was checked with good color reappearance.

[0109] Printing and UV irradiation were performed to CF102 (canon product) which is an OHP film for ink jets about the watercolor pigment ink of the example of comparison 1 ink set 2 like the example 1. In CF-102 which are the film of OHP for ink jets, the amount which can absorb water color ink was measured with 3×10^6 pl/cm² (=30 ml/m²), and has fully exceeded the amount of ink given by 1 color poor printing. Moreover, although the measurement with the contact angle exact for water absorption over pure water was difficult, the value was estimated at 20 or less degrees from the configuration in early stages of a drop. Thus, it changed into the condition that the pigment particle deposited on the film front face, and obtained OHP of coalescence of a drop was inadequate. This became a cause, and dispersion of the transmitted light was intense and very inadequate for the transparency as an OHP. The measurement result of a transparency spectrum is shown in Table 19.

[0110]

[Table 19]

表 19 (透過スペクトル測定結果)

	Y		M		C	
	吸収域	透過域	吸収域	透過域	吸収域	透過域
波長 (nm)	400	600	550	650	650	480
透過率	0.12	0.70	0.22	0.65	0.25	0.75

[0111] In Table 19, the thing with the large value in an absorption region has inadequate coalescence of a dot, and it is because the very small field which light penetrates directly remains. On the other hand, in the transparency region, dispersion of light was reducing permeability.

[0112]

[Effect of the Invention] According to this invention, printing which absorptivity forms in an ink layer with high transparency to the base material which is not enough as opposed to an unabsorbent base material using the ink in which the pigment was distributed into an aqueous medium is attained.

[0113] When a base material is a base material of light transmission, it becomes possible to perform printing which has little lightfastness and transparency of dispersion. Moreover, in printing in pigment ink, adhesion force is excellent and an improvement of these engine performance made into the fault in conventional ink jet watercolor pigment ink also in saturation and lightness is made.

[Translation done.]

(3)

する濡れ性が悪い場合には、インクの表面張力を低下させる必要があった。また、そうした場合でも均一なインク層を高解像度で得ることは難しく、得られた印刷物の用途は限定されたものとなる場合があった。

【0007】本発明は、かかる紫外線硬化型インクをインクジェット法による印刷に用いる場合における問題点に鑑み、従来のインクと異なり、硬化後のインクの被印刷材への付着力が高く、被印刷材が光透過性であるならば透明性に優れた印刷を、また被印刷材が光反射性であるならば光沢、彩度の高い印刷を可能とするインクジェット印刷を提供することをその目的とする。

【0008】
 【課題を解決するための手段】本発明のインクジェット印刷方法は、水性媒体中に、少なくとも顔料、水性性の紫外線重合性物質及び水溶性の光重合開始剤を含有するインクを用いて、被印刷材にインクジェット印刷を行う印刷方法において、被印刷材の被印刷面に1色のインクのインク層の多数を付着させて該被印刷面に1層のインク層で覆うように印刷する場合を1色への印刷としたとき、該被印刷面の純水に対する静的接触角 γ_w が

【0009】
 【数1】 $\gamma_w \leq 60^\circ \cdots (1)$
 を満足し、かつ、1色への印刷する際に付与する単位面積あたりのインク体積を V_L (pl/cm^2)、*

表1 (1色への印刷に付与するインク量 V_L)

解像度	1ドットの被印刷面積	VL	
		ml/cm ²	pl/cm ²
180 dpi	200 pl	10.0	1.00×10^6
300 dpi	120 pl	16.7	1.67×10^6
360 dpi	80 pl	16.0	1.60×10^6
600 dpi	40 pl	22.3	2.23×10^6
720 dpi	36 pl	28.1	2.81×10^6

【0015】一方、インクからの紫外線硬化物を良好な状態で被印刷材の被印刷面に形成するには、被印刷材の被印刷面上に供給されたインクのうちの十分な量が被印刷材中に吸収され、被印刷面上に残存している必要があり、上記表1の各数値で示す条件で印刷を行う場合のVR (被印刷材が吸収し得るインク (液相) の体積) の値は、上記のVLよりも十分に小さい値を取る必要がある。そこで、本発明においてはVLに対して十分に小さな、すなわち上記表(2)を満たすVRを提供できる被印刷材とインクとの組み合わせが用いられる。なお、表1に示す通り、VLはプリンタの解像度と1ドット当りのインク滴の体積に主に依存する量であり、これらの条件を変化させることで調整できる。なお、良好なベタ印刷が達成されているかどうかは、肉眼及び顕微鏡下に

*前記被印刷面が吸収し得るインクの容積をVR (pl/cm^2) としたとき、

【数4】 $VR \leq VL \times 0.5 \cdots (2)$

の条件を満たすインクと被印刷材とを用いて印刷を行うことを特徴とする。

【0011】本発明によれば、水性の紫外線硬化型インクを用いたインクジェット印刷において非インク吸収性の被印刷材を用いた場合でも、良好な被印刷材の被印刷面におけるぬれ性を得ることができ、良好なインクジェット印刷が可能となる。

【0012】

【発明の実施の形態】本発明における「1色への印刷」は、上記の通り1色のインクを用いて形成される1つのインク層が、被印刷材の被印刷面全面を覆うように形成されるのに必要な印刷条件での印刷をいい、例えば、同一被印刷材を用いて所定厚の均一なインク層を形成する場合のインク付与量を式で計算すると、以下の表1に整理した通りとなる。

【0013】

【数5】1色への印刷に付与するインク量=解像度 \times 解像度 \times 1ドットの液滴体積/面積 (インク平方)
 【0014】
 【表1】

おいて、面全体が均一な濃度となり、かつ色材粒子の凝集による濃度の高い微小粒子が観察されないことにより判断できる。

【0016】また、VRは、インク液滴の大きさを種々変えて1色へ3色への印刷を被印刷材に対して行い、10分後における表面の乾燥状態から単位面積当りのインク吸収量として計測して得ることができる数値である。
 【0017】なお、表1に示した解像度及びインク滴についての数値は1色への印刷における代表的な条件を示したものであり、これらに限定されない。また、本発明における1色への印刷に関する式(2)の条件は、被印刷材とインクとの組み合わせに関する条件を規定するものであり、実際の印刷では2色以上のインクでの印刷、領域へのベタ印刷、ベタ印刷とならないドットでの印刷、

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【0022】

表2 (汎用ガラスチップの静的接触角)

ガラスチップ名称	純水の静的接触角 (度)
低密度ポリエチレン	94
ポリ塩化ビニル	87
ポリ塩化ビニリデン	80
ポリテトラフルオロエチレン	108
ポリエチレンテトラフルオレート	76~81
ポリメチルメタクリレート	80
6-6ナイロン	70~72
ポリスチレン	91

【0023】こうしたことから、ガラスチップのシートに、少なくとも水を含有するインクで印刷するために、インクに界面活性剤を添加する方法によってインク自身の表面張力を下げてシート上でのインクの濡れ広がり大きくする方法が取られて来た。そして同時に、(1)メチルエチルケトン、マシロラクトンのような水と混和でき、かつガラスチップにも親和性のある有機溶媒を水と混ぜてインクの溶媒成分として用いる、(2)エチルアルコール、イソプロピルアルコールのような速乾性の溶媒をインクに添加して、シート上でのインクの溶媒成分の蒸発を速くし、粘度を上昇させて不均質な収収を防止する、などの方法も併用された。しかしながら、これらの方法では、コードを印刷するような大きなドットによる低い解像度の画像は描けても、精密な画像、あるいは高いぬれ性を必要とするベタ印刷には、その仕上りの精度は全く不十分なのであった。

【0024】本発明では、好ましくは、(1)式の関係を満足することができ、被印刷材を選択し、あるいは表面処理で得ることによって高解像度の望ましい印刷結果が得られる、とりわけ、光透過性の被印刷材への透明な印刷を目的とする場合には、被印刷材の表面の平滑性を失わない範囲で、あるいは、表面の平滑性を増やすことを求めて被印刷材の表面処理を行うことが効果的である。

【0025】インクと基材が上記の式(1)及び(2)で表される範囲にあると、ノズルから飛翔し着弾したインクの液滴は、被印刷材の被印刷面上において広がり、隣接した液滴が効果的に合体して平滑な液滴層を形成でき、この関係からはずれなく、液滴は収縮して液滴相互に合体して均一な液膜を形成しない場合が生ずる。その結果、画像としての平滑感、均一感が得られ、また透明性を要求する場合には、光散乱を非常に大きくするので、實際上透明性は失われる場合が生じてくる。
 【0026】(1)式を満足させる方法としては、被印

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 樹脂を構成し得るシート形状等の所望の形状の基材の被印刷面となる表面に水性液体に対するγ。を上昇させるように表面処理を行う方法が好ましく、このことにより、インクの濡れ拡がりは、保証される。すなわち、水性インクの吸収性を持つ水性高分子化合物、金属化合物などを条件(1)の範囲で使用することが効果的である。

【0027】(1)式を満足させる別の方法としては、酸溶フラスコ酸化、電子ビーム照射、200nm近傍の遠紫外線照射、フレーム(火焔)処理、酸化焙焼、酸化アルミなどの蒸着、スパッタリングなどの物理的な表面処理が有効である。

【0028】紫外線硬化性の物質を用いる本願発明の水性インクでは、例えば、以下の2通りのインク材料構成とそれに対応した印刷方法を採用することができる。印刷方法としては、溶剤分の除去工程(蒸発、加熱乾燥、水沈)を含んでいる。

【0029】第1のインク材料構成は、色材としての顔料、水、液状の水溶性重合性化合物及び水溶性光開始剤から構成される組成物である。ここでは、液状の水溶性重合性化合物が溶解性をも発現するので、一般の水系インクジェットインクで使用されるような、不揮発性親水性溶剤を使用しない。第2のインク材料構成は、色材としての顔料、水、水溶性有機溶媒、液状の水溶性紫外線硬化剤、水溶性光開始剤から構成される組成物である。

【0030】以下、各成分について説明する。

【0031】＜紫外線＞によって硬化する水溶性重合性物質＞紫外線によって硬化する水溶性重合性物質として、単官能あるいは多官能の重合性化合物が使用でき

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 る。その中でも、1分子中に2以上のアクリロイル基を有し、水に対する溶解度が10重量%以上である化合物が望まれる。しかもこれまでに溶解し、粘度が低く、光重合性があり、硬化膜の物性にも優れた物質は極めて値がしかられていなかった。水に溶解する多官能の物質のうち、ポリエチレングリコール構造を有する化合物は、代表的な物質である。しかし、これらは水溶性はあっても、塗膜の耐水性が悪く、よく密着する基材にも制限がある。多価アルコールのエピクロヒドリン付加化合物から誘導されるアクリル酸エステル、一般的にはエポキシアクリレートと呼ばれる化合物群は水溶性が高く、紫外線硬化速度も早く、塗膜物性にも優れるが、多数の水酸基を有するがゆえに、粘度がやや高いという特徴がある。このためにインク中での使用が制限される場合がある。

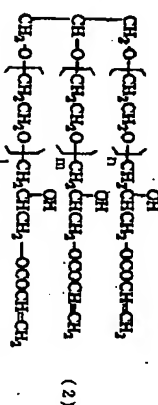
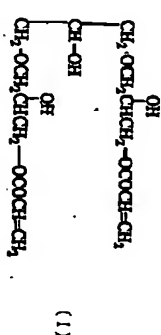
【0032】液状を呈し、親水性で吸湿性が強く、不揮発性の紫外線重合性化合物を用いることで、不揮発性有機溶媒を含有しない第1の構成の水性インクジェットインクを構成することが可能となる。

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 【0033】多官能性の重合性化合物の一つは、多価アルコールの(メタ)アクリルエステルである。このグループで水溶性の化合物としては、ポリエチレングリコールのアクリル酸エステルである。ポリエチレングリコール#200ジアクリレート及びポリエチレングリコール#200ジアクリレートなどが挙げられる。更に、以下の化合物に代表される水溶性のエポキシアクリレートも利用できる。

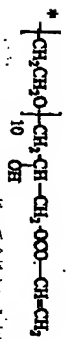
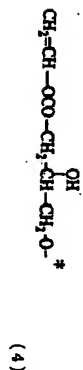
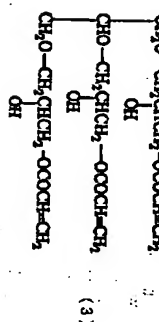
【0034】

〔化1〕

(6)



$n+m+i=1 \sim 16$



性、重合性という本発明の基本的な要素の一部を持ち、

などを挙げることができる。

【0035】ノニオン性の水溶性を有する重合性化合物

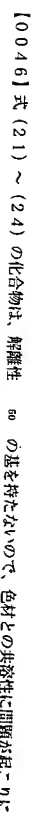
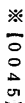
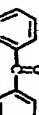
30
 を利用することもでき、このような重合性化合物として、単糖類、2糖類など2以上の水酸基を有するポリオール(メタ)アクリル酸エステル；トリエタノールアミン、ジエタノールアミン、トリスヒドロキシアミノメタン、トリスヒドロキシアミノエタンなどの(メタ)ア

クリル酸エステルを挙げることができる。これらは水溶

【0036】下記構造のアクリレートは、高反応性でかつ低粘度であるので本発明におけるインクの成分として特に好ましく用いられるものである。

【0037】

〔化2〕



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289、アジドレジン315、アジドレジン317、
7、ダイレクタレジンF1、ダイレクタレジンF4、ダイレ
クタレジンF13、ダイレクタレジンF17、ダイレクタレ
ジンF23、ダイレクタレジンF28、ダイレクタレジンF3
1、ダイレクタレジンF62、ダイレクタレジンF79、ダ
イレクタレジンF81、ダイレクタレジンF89、ダイレク
トラレジンF227、ダイレクタレジンF240、ダイレクタ
レジンF242、ダイレクタレジンF243、などが適用で
きる。

【0065】シアン染料としては、アジドブルー9、
アジドブルー22、アジドブルー40、アジドブ
ルー59、アジドブルー93、アジドブルー10
2、アジドブルー104、アジドブルー113、ア
ジドブルー117、アジドブルー120、アジドブ
ルー167、アジドブルー229、アジドブルー
234、アジドブルー254、ダイレクタレジン6、
ダイレクタレジン22、ダイレクタレジン25、ダイレ
クタレジン71、ダイレクタレジン78、ダイレクタ
ルー86、ダイレクタレジン90、ダイレクタレジン1
06、ダイレクタレジン199、などを適用できる。

【0066】これらの既存の色材だけではなく、新規に
開発された化合物の中でも色相、耐光性、耐水性を満足
するものであれば、大きな困難なく本発明の構成におい
て適用可能である。

【0067】インク中の顔料の顔料の純分としての重量
は0.5ないし10.0重量%とすることが好ましい。
また、染料を併用する場合には、0.1〜5重量%とす
ることが好ましい。

【0068】＜インク中の顔料の粒子径＞従来のインク、
塗料、ガラスシールへの顔料の使用においては、顔料の
粒子径を約0.2ミクロン以下とすると透明性が非常に
向上し始めるといわれた。しかし平均粒子径を0.2
ミクロン以下にしただけの一般のインクジェット顔料
インクでは、極めて透明性が悪い結果となる場合があ
る。これに対して本発明の方法によれば、顔料の粒子径
に基づく透明性に加えて、紫外線重合性化合物の硬化に
よって得られた透明性が発現する。したがって、本発明の
印刷法をとるならば、顔料粒子の平均粒子径は25nm
〜250nm程度の範囲に入っていればよい。この範囲
は印刷物の用途にも依存するが、一般的な意味では十分
に透明と言える印刷物を与える。もちろん顔料粒子サイ
ズは小さいことが望ましいが、本発明の方法を用いるな
らば、粒子径を100nm以下にすることはいつも必要
とはならない。

【0069】＜インクの作成方法＞インクは、使用する
原材料をいかなる順序で混合してもよいが、混合は速や
かに不均一な状態を長く保持することなく行う。また顔
料分散体を使用する場合には、均一性を損なわないよう
にさらによく攪拌を行う。

【0070】＜ブリッジシステム＞本発明を実施するブ

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リッジシステムにおいては、インクジェット機械に紫外
線照射装置が必要である。紫外線照射装置は、典型的に
図1に例示されるような位置に配置される。紫外線は、
ブリッジシステムを出た記録紙に上面あるいは下
面、あるいは、上下両面から照射される。透明な基材の
場合にはそのような選択はもたら可能である。ブリッ
ジヘッドから照射エリアへの時間間隔は、インクが完全
に記録紙に浸透してしまいう前の、インク成分が均一に
ある状態を保っている時間域で行われるのが最良である。
その意味で基材の浸透能力が抑制された本発明の印刷条
件では、そのタイミングの許容範囲は大きい。たとえ記録
基材の種類は多くても、その浸透が抑制されているので
硬化的な照射は確実に行うことが可能となる。

【0071】＜紫外線照射ランプ＞紫外線照射ランプ
は、水銀の蒸気圧が、点灯中で1〜10Paであるよう
な、いわゆる低圧水銀ランプ、高圧水銀ランプ、蛍光
管が塗布された水銀管などが好ましい。これらの水銀ラ
ンプの紫外線領域の発光スペクトルは、184nmから4
50nmの範囲であり、黒色あるいは、着色されたイン
ク中の重合性の物質を効率的に反応させるに適してい
る。また、電線をブリッジに搭載する上でも小型の電線
を使用できるので、その意味でも適している。水銀ラ
ンプには、メタルハライドランプ、高圧水銀管、超高压水銀
管、クセノンランプ、シアンランプ、ダイオードUVランプ、
UVレーザーなどがあり使用されており、発光波長領域とし
ては上記範囲を含むので、電圧サイズ、入力強度、ラン
プ形状などが許されれば基本的には適用可能である。光
源は用いる媒体の感度にも合わせて選択する。

【0072】必要な紫外線強度は、2〜50mW/cm
2の程度が重合速度の位置から望ましい。計算照射量が
不足していると同質したインクの記録紙への付着力が十
分に出ない。また、カラー記録では、耐水性が十分に
出ない、などの本発明の目的である。印刷インクの堅牢性
において不足が生じることとなる。

【0073】＜印刷工程＞本発明の印刷法は基本的に以
下の工程を有することが好ましい。

- (1) 基材にインクジェットランプで印刷する工程
- (2) 基材に紫外線を照射しインク中の重合性物質を重
合する工程

(3) 基材中の溶媒成分を除去する工程
ここで工程(3)は、(2)の前であっても後であつて
もよい。

【0074】本発明においてはインク受容層のインク受
容能力が十分でなく溶媒が表面近傍に残留しているため
未蒸発の溶媒成分を除去するために(3)の工程を用い
ることが好ましい。

【0075】ただし、先に述べたように、水溶性で比較
的揮発性の高い有機溶媒を用いる場合、あるいは水溶性
有機溶媒を用いない場合には(3)の工程がなくてもよ
い場合もある。溶媒成分の除去には、マイクロ波乾燥装

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置、遠赤外線ランプ、などの加熱方法を採用することが
できる。また、不揮発性の溶媒を使用する場合には、紫
外線硬化後にもそれが水に対して抵抗性のある基材
であるならば、水洗を行うことが最も簡便かつ効果的
である。

【0076】インクを紫外線で固着させることによ
て、良好な定着、搬送性、耐水性などが得られる。それ
とともに用紙自体のカラー、コンパイルなどの変形が抑制

表3 (イエローインク1)

成分	組成 (重量%)
顔料分散液 [*] (濃度 18%)	顔料分 3.5
水溶性重合性物質 [*] [式 (17)]	15.9
水溶性重合性物質 [*] [式 (6)]	4.0
水溶性重合性物質 [*] [式 (6)]	13.0
水溶性光重合開始剤 [*] [式 (21) : n=4]	0.5
水	63.1

* ビジメントイエロー74分散体：平均粒子径：110nm、分散剤：水溶性
のポリウレタン樹脂 (数平均分子量3000)

【0079】

※ ※ [表4]

表4 (マゼンタインク1)

成分	組成 (重量%)
顔料分散液 [*] (濃度 14%)	顔料分 2.5
水溶性重合性物質 [*] [式 (17)]	15.3
水溶性重合性物質 [*] [式 (6)]	4.0
水溶性重合性物質 [*] [式 (6)]	13.0
水溶性光重合開始剤 [*] [式 (21) : n=4]	0.5
水	64.7

* ビジメントレッド122分散体：平均粒子径：90nm、分散剤：水溶性の
ポリウレタン樹脂 (数平均分子量3000)

【0080】

★ ★ [表5]

表5 (シアニンク1)

成分	組成 (重量%)
顔料分散液 [*] (濃度 16%)	顔料分 3.0
水溶性重合性物質 [*] [式 (17)]	17.0
水溶性重合性物質 [*] [式 (6)]	4.0
水溶性重合性物質 [*] [式 (6)]	13.0
水溶性光重合開始剤 [*] [式 (21) : n=4]	0.5
水	62.5

* ビジメントブルー15：3分散体：平均粒子径：75nm、分散剤：水溶性
性のポリウレタン樹脂 (数平均分子量3000)

【0081】

※ ※ [表6]

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表6 (ブラックインク1)

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成分	組成 (質量%)
顔料分散液 [*] (濃度 2.0%)	5.0
水	20.0
水溶性紫外線重合性オリゴマー「式(17)」	4.0
水溶性重合性物質「式(6)」	13.0
水溶性光重合開始剤「式(21) : n=4」	0.5
水	57.5

* ビタミントトラック7分散体：平均粒子径：95nm、分散剤：水溶解性のポリウレタン樹脂 (数平均分子量3000)

インク処方例2

(インクセット2：水溶性有機溶剤を含むインク)

* [0082]

* [表7]

表7 (イエローインク2)

成分	組成 (質量%)
顔料分散液 (濃度 1.5%)	3.0
水	17.0
水溶性紫外線重合性オリゴマー「式(8)」	4.0
水溶性紫外線重合性オリゴマー「式(7)」	8.0
水溶性光重合開始剤「式(22)」	0.5
水溶性溶剤 2-ヒロリドン	10
ジエチレングリコール	5
水	52.5

* ビタミントイエロー93分散体：平均粒子径：135nm、分散剤：アルコール可溶性のアクリル樹脂 (数平均分子量5300)

[0083]

* [表8]

表8 (マゼンタインク2)

成分	組成 (質量%)
顔料分散液 (濃度 1.5%)	3.5
水	19.8
水溶性紫外線重合性オリゴマー「式(8)」	4.0
水溶性紫外線重合性オリゴマー「式(7)」	8.0
水溶性光重合開始剤「式(22)」	0.5
水溶性溶剤 2-ヒロリドン	10
ジエチレングリコール	5
水	49.2

* パーマネント カルミン (Permanent Carmine) GG-2105 (ビタメントレッド238) 分散体：平均粒子径：115nm

[0084]

[表9]

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表9 (シアングリーン2)

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成分	組成 (質量%)
顔料分散液 (濃度 1.5%)	2.5
水	14.2
水溶性紫外線重合性オリゴマー「式(8)」	4.0
水溶性紫外線重合性オリゴマー「式(7)」	8.0
水溶性光重合開始剤「式(22)」	0.5
水溶性溶剤 2-ヒロリドン	10
ジエチレングリコール	5
水	55.8

* ビタミントブルー15：3分散体：平均粒子径：75nm、分散剤：アルコール可溶性のアクリル樹脂 (数平均分子量5300)

[0085]

* [表10]

表10 (ブラックインク2)

成分	組成 (質量%)
顔料分散液 (濃度 1.9%)	5.0
水	21.3
水溶性紫外線重合性オリゴマー「式(8)」	4.0
水溶性紫外線重合性オリゴマー「式(7)」	8.0
水溶性光重合開始剤「式(22)」	0.5
水溶性溶剤 2-ヒロリドン	10
ジエチレングリコール	5
水	46.2

* ビタミントブラック7分散体：平均粒子径：95nm、分散剤：アルコール可溶性のアクリル樹脂 (数平均分子量5300)

インク処方例3

(インクセット3：水溶性有機溶剤を含むインク)

* [0086]

* [表11]

表11 (イエローインク3)

成分	組成 (質量%)
顔料分散液 (濃度 1.5%)	3.0
水	17.0
水溶性紫外線重合性オリゴマー「式(8)」	5.0
水溶性紫外線重合性オリゴマー「式(5)」	7.0
水溶性光重合開始剤「式(19)」	0.5
水溶性溶剤 2-ヒロリドン	10
ジエチレングリコール	5
水	52.5

* ビタミントイエロー128分散体：平均粒子径：123nm、分散剤：トオスアノールR610 (HLB=12.6、東邦化学製)

[0087]

[表12]

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表12 (マゼンタインク3)

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成分	組成 (質量%)
顔料分散液 (濃度 1.5%)	顔料分 3.5
水溶性紫外線重合性オリゴマー「式(8)」	19.8
水溶性紫外線重合性オリゴマー「式(5)」	5.0
水溶性光重合開始剤「式(19)」	7.0
水溶性溶剤 2-ヒロリドン	0.5
ジエチレングリコール	10
水	5
	49.2

*) ビジメントレフト122分散体：平均粒子径：140nm；分散剤：フオス
フアノールRE610 (HLB=12.6、東邦化学製)

[0088]

表13 (シアンインク3)

* * [表13]

成分	組成 (質量%)
顔料分散液 (濃度 1.5%)	顔料分 2.5
水	14.2
水溶性紫外線重合性オリゴマー「式(8)」	5.0
水溶性紫外線重合性オリゴマー「式(5)」	7.0
水溶性光重合開始剤「式(19)」	0.5
水溶性溶剤 2-ヒロリドン	10
ジエチレングリコール	5
水	55.8

*) ビジメントブルー15：3分散体：平均粒子径：110nm；分散剤：フオ
スフアノールRE610 (HLB=12.6、東邦化学製)

[0089]

表14 (ブラックインク3)

※ * [表14]

成分	組成 (質量%)
顔料分散液 (濃度 1.9%)	顔料分 5.0
水	21.3
水溶性紫外線重合性オリゴマー「式(8)」	5.0
水溶性紫外線重合性オリゴマー「式(5)」	7.0
水溶性光重合開始剤「式(19)」	0.5
水溶性溶剤 2-ヒロリドン	10
ジエチレングリコール	5
水	46.2

*) ビジメントブラック7分散体：平均粒子径：95nm；分散剤：フオスフ
アノールRE610 (HLB=12.6、東邦化学製)

[0090] 実施例1

75ミクロンのポリエチレンテレフタレートフィルムを
基材とし、これに架橋性水溶性ポリアミド樹脂である、
60 100部：架橋剤=100：2 (重量部)、フイア

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バーコート#10にて塗布し、20℃にて15分乾燥し
た。これによって膜厚4ミクロンの親水性ポリアミド樹
脂層を有する被印刷材1を調製した。このフィルム表面
の純水に対する接触角は30度であった。このフィルム
が吸収し得るインク量は、印刷試験の結果およそ $1 \times 10^5 \text{ p l / cm}^2$ ($=1 \text{ ml / m}^2$) であった。塗膜は
良好な耐水性を示した。

[0091] 図1に示した配置構成のインクジェットプ
リンタに紫外線照射ランプを搭載した装置を用いて印刷
試験を行った。この実験装置では、パノラマウェット方式
のプリンtheadを用い、1色1ヘッドにおいて印刷す
るインク量は、 $2.2 \times 10^6 \text{ p l / cm}^2$ と設定した。
搭載したランプは、ウシオ電気製低圧水銀ランプUL1
-5DQ (入力50W、90V、0.6A) である。イ
ンクが付与されてから紫外線照射領域に入るまでの時間
は、およそ7秒、紫外線照射を受けている時間はおよそ
*

表15 (透過スペクトル測定結果)

波長 (nm)	Y		M		C	
	吸収域	透過域	吸収域	透過域	吸収域	透過域
透過率 (表面処理あり)	400	600	550	650	650	480
透過率 (表面処理なし)	0.03	0.95	0.1	0.97	0.1	0.95
	0.15	0.70	0.25	0.65	0.20	0.55

[0095] なお、表面処理なしの場合には、インク散
漫の合が進まず、平滑な被膜が形成されなかったの
で、透過率を評価するには、印刷物の均一性自体が極め
て不完全な状態であった。

[0096] 実施例2

75ミクロンのポリエチレンテレフタレートフィルムを
基材とし、これにポリエチレングリコール樹脂 (分子重
80,000) とグリオキザールの混合物 (ポリエチレ
ングリコール：グリオキザール=、100：3 (重量
部)) をフイアバーコート#20にて塗布し、摂氏1
25度にて20分乾燥した。これによって膜厚10ミク
ロンのポリエチレングリコール樹脂層を有する被印刷材
2を調製した。この樹脂表面は架橋によって耐水性のあ

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* よそ10秒である。

[0092] インクセット1を使用し、被印刷材1にカ
ラーの1色 (YMC) のべたバーンをそれぞれ印刷
し、紫外線照射を行った。得られた印刷物は、マイクロ
波照射装置内にて蒸発乾燥し所望の印刷物を得た。これ
らの印刷物を用いて透過スペクトル測定を行った。なお
比較として被印刷材製造例1における基材に対して表面
処理を行わずに上記と同様に印刷を行って印刷物を作成
して透過スペクトルを測定した。以上の測定結果を表1
5に記載した。

[0093] 好ましい透明性を示すということは、透過
率において、色材自身が吸収すべき波長域では0にな
り、吸収しない波長領域では1になることである。

[0094]

[表15]

る表面であり、かつ純水に対する接触角は15度であっ
た。また吸収し得るインク量は、 $4 \times 10^6 \text{ p l / cm}^2$
であった。

[0097] インクセット2と被印刷材2を用い、実施
例1と同様にしてカラーの1色 (YMC) のべたバー
ン印刷し、紫外線照射を行った。得られた印刷物は、遠
赤外線乾燥機にて蒸発乾燥し所望の印刷物を得た。更
に、基材 (表面処理なし) を用いて同様の操作により印
刷物を得た。これらの印刷物を用いて透過スペクトル測
定を行い結果は表16に記載した。

[0098]

[表16]

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表16 (透過スベクトル測定結果)

	Y		M		C	
	吸収域	透過域	吸収域	透過域	吸収域	透過域
波長 (nm)	400	600	550	650	650	480
透過率	0.05	0.92	0.08	0.94	0.08	0.94
(表面処理あり)						
透過率	0.17	0.82	0.23	0.70	0.22	0.80
(表面処理なし)						

【0099】なお、表面処理なしの場合には、インク液滴の合一が通まず、平滑な液膜が形成されなかったもので、透過率を算出するには、印刷物の均一性自体が極めて不完全な状態であった。

【0100】実施例3

1. 1mmの厚さの7059ガラス板を基材としてその表面を紫外線照射装置にて5分照射し、次いでアルカリ性洗剤で超音波洗浄し、その後水洗乾燥して被印刷材を得た。この被印刷材の表面処理前の純水に対する接触角は13度であった。この被印刷材を用いて以下の工程で印刷を行った。

【0101】図2に示すような幾み性のない板上の基材に印刷可能で、かつ、基材の上下から紫外線照射できるように配置したバブルジェット印刷装置を準備した。*

表17 (透過スベクトル測定結果)

	Y		M		C	
	吸収域	透過域	吸収域	透過域	吸収域	透過域
波長 (nm)	400	600	550	650	650	480
透過率	0.05	0.96	0.09	0.95	0.7	0.95

【0104】実施例4

75ミクロンのエチレンテレフタレートフィルムを基材とし、これにポリビニルアルコール樹脂（ポリマーA）を成分重量50、000酸化度85%の架橋剤として水溶性ポリエポキシドである、デチコールEX314、及び架橋反応触媒として、ホフマン化亜鉛塩を添加して（デチコールEX314：ホフマン化亜鉛塩酸塩：100：5（低当量））、ウイザーバーコート#30にて塗布し、摂氏120度にて15分乾燥した。これによって図2に示すような幾み性のない板上の基材に印刷可能で、かつ、基材の上下から紫外線照射できるように配置したバブルジェット印刷装置を準備した。*

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* 前には254nmの光源、下部には365nmの光源を配置した。これを用いて、実施例3のインクを使用し、基材3に印刷試験を行った。搭載したランプは、上下とも中心波長近傍において5mW/cm²の出力特性を有する高圧水銀灯である。インクセット3のインクを各々使用し、被印刷材3に、カラーの1色（YMC）のべたパターンを印刷し、紫外線照射を行った。

【0102】得られた印刷物（着色ガラス板）は水洗した後、ワイコロ波照射装置内にて蒸気乾燥させた。こうして得られた着色ガラス板を用いて透過スベクトル測定を行った。これらの結果は表17に記載した。

【0103】

【表17】

が吸収し得るインク量は、印刷試験の結果およそ1×10⁶g/cm²（=10ml/m²）であった。塗膜は良好な耐水性を示した。

【0105】実施例1と同様に、図1に示した構成の装置を用いて印刷試験を行った。使用したインクは、インクセット2である。実施例1と同様に印刷及び紫外線照射を行った。得られた印刷物は、熱風オーブン内にて蒸気乾燥し所望の印刷物を得た。これらの印刷物を用いて透過スベクトル測定を行った。以上の測定結果を表18に記載した。

【0106】

【表18】

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表18 (透過スベクトル測定結果)

	Y		M		C	
	吸収域	透過域	吸収域	透過域	吸収域	透過域
波長 (nm)	400	600	550	650	650	480
透過率	0.03	0.95	0.1	0.97	0.1	0.95

【0107】実施例5

基材表面にポリエチレン層を印刷したレジコント紙に親水性ポリエタレン樹脂である、バイロナル（東洋紡製）をウイザーバーコート#30にて塗布し、120℃にて15分乾燥し被印刷材5を得た。なお、ポリエタレン樹脂層の厚さは膜厚13μmであった。この記録紙表面の純水に対する接触角は60度であった。また記録紙が吸収し得るインク量は、印刷試験の結果およそ0.5×10⁶g/cm²（=5ml/m²）であった。

【0108】実施例1と同じ装置を使用し、インクセット3と被印刷材5を用いて、YMCRGBの7色のべたパターンを印刷した。得られた印刷物は、加熱炉に3分投入して蒸気乾燥を行った。これらの印刷物を用いて、画像濃度、色彩測定（彩度、明度、色相）を行った。また、市販のイエローカーににて画像濃度を塗り、耐性を評価した。その結果、良好な色彩再現と、高い耐湿性能が確認された。

【0109】比較例1

表19 (透過スベクトル測定結果)

	Y		M		C	
	吸収域	透過域	吸収域	透過域	吸収域	透過域
波長 (nm)	400	600	550	650	650	480
透過率	0.12	0.70	0.22	0.65	0.25	0.75

【0111】表19において吸収域での値が大きいのは、ほとんどの場合が十分に光が直接透過する微小領域が残っているからである。一方、透過域では、光の散乱が透過率を低下させていた。

【0112】

【発明の効果】本発明によれば、水性媒体中に顔料が分散されたインクを用いて、非吸収性基材に対して、あるいは吸収性が十分でない基材に対して透明性の高いインク層で形成する印刷が可能となる。

【0113】基材が光透過の基材である場合には散乱の少ない、透光性と透明性を兼ね備えた印刷を行うことが可能となる。また、顔料インクによる印刷において、付着力が優れ、彩度、明度においても従来のインクジェット水性顔料インクにおいて、欠点とされていたこれらの

性能の改善がなされる。

【図面の簡単な説明】

【図1】本発明の水溶性架橋変性インクを用いたインクジェット印刷法を適用し得るプリンタの概略を示す図である。

【図2】本発明の水溶性架橋変性インクを用いたインクジェット印刷法を適用し得るプリンタの概略を示す図である。

【符号の説明】

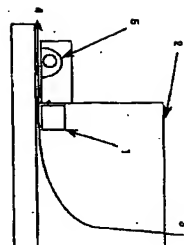
- 1 インクジェットプリントヘッド
- 2 プリンタ本体
- 3 被印刷材
- 4 吐出される被印刷材
- 5 紫外線ランプ

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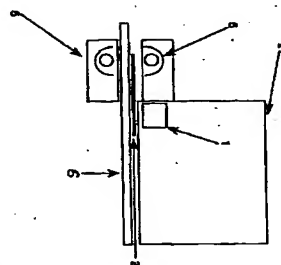
6 被印刷材の搬送台

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【図1】



【図2】



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